

# How to reconcile Information theory and Gibbs-Hertz entropy for inverted populated systems

Alessio Gagliardi<sup>1</sup>, Alessandro Pecchia<sup>2</sup>

(1) *Technische Universität München,  
Electrical Eng. and Information Tech.,  
Arcisstr. 21 80333 München (Germany). alessio.gagliardi@tum.de  
Tel: (+49) 89 289 26931.*

and

(2) *CNR, Via Salaria Km 29,  
600, 0017 Monte Rotondo (Italy)*

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In this paper we discuss about the validity of the Shannon entropy functional in connection with the correct Gibbs-Hertz probability distribution function. We show that there is no contradiction in using the Shannon-Gibbs functional and restate the validity of information theory applied to equilibrium statistical mechanics. We show that under these assumptions, entropy is always a monotone function of energy, irrespective to the shape of the density of states, leading always to positive temperatures even in the case of inverted population systems. In the second part we assume the validity of the Shannon entropy and thermodynamic temperature,  $T = dE/dS$ , extended to systems under non-equilibrium steady state. Contrary to equilibrium, we discuss the possibility and meaning of a negative temperature in this case. Finally we discuss on Carnot cycles operating with a non-equilibrium bath possessing a negative temperature and leading to apparent efficiencies larger than one, due to a wrong accounting of all the energy and entropy fluxes present in the system, including the external driving forces.

## I. INTRODUCTION

Recently a large debate has started about the existence of systems - especially systems with upper bounded density of states that can lead to inverted population conditions even in equilibrium - that turns to have negative temperatures [1]. The idea of a negative temperature is an old concept, elaborated by many authors [2–4]. It comes from the possibility that the derivative of entropy,  $S$ , with respect to internal energy,  $E$ , exhibits a negative slope hence, from its thermodynamical definition, temperature becomes negative.

In their paper [5] Dunkel et al. showed that this is not correct and that the entire idea of negative temperature stems from the wrong assumption about the entropy functional (Boltzmann-Gibbs-Shannon) for a system in a microcanonical ensemble. Subsequently, another paper [6] has been published to strengthen this point, fundamentally concluding with these three important findings:

- A system which stays in an inverted population at equilibrium state must be in a microcanonical ensemble;
- The rigorous entropy functional is the Gibbs-Hertz entropy functional;
- For this choice of the entropy the temperature computed as derivative of entropy w.r.t. internal energy remains always positive.

In particular, their conclusion is also that the entropy functional has not the shape of an information entropy functional represented by the Shannon entropy and thus

information theoretical concepts should be carefully considered before being applied to thermodynamics. They even suggest that the Gibbs-Hertz entropy should be included as a "new" information measure if we want to include the microcanonical ensemble within the formalism of information theory.

Although their derivation is completely right, we demonstrate in this work that it does not exclude an information theoretical approach to statistical physics. Furthermore we show that the Shannon standard entropy functional works and represents a general functional, at least valid in equilibrium condition and in non-equilibrium steady state (NESS), hence there is no need to invent a new information measure. Finally, in the last part, we briefly discuss under which conditions a negative temperature is still possible and the implications on Carnot cycle efficiencies. However, the last part does not include rigorous general demonstrations, but rather a collection of several results and then should be regarded as a suggestion for future investigations.

## II. ENTROPY: WHICH FUNCTIONAL?

Before starting we make the same assumptions as in [6], namely that the system is strictly isolated (microcanonical ensemble), and is described by an Hamiltonian,  $H(\xi, Z)$ , where  $\xi$  denotes the microscopic state and  $Z = (Z_1, \dots)$  comprises external control parameters. The system conserves energy  $E$  and the energy is bounded from below  $E \geq 0$ . The probability distribution function (PDF) over the density of states (DOS) of the phase

space is assumed to be uniform over a subset of the possible states  $\xi$  of the system. However, this leaves an uncertainty about the domain on which this uniform distribution is different from zero. In the literature several possible choices are discussed, the microcanonical density operator (MDO) defined as:

$$\rho_M(\xi|\bar{E}, Z) = \frac{\delta(\bar{E} - H(\xi|Z))}{\omega(\bar{E}, Z)}, \quad (1)$$

or the following:

$$\rho_C(\xi|Z; \bar{E}) = \frac{\theta(\bar{E} - H(\xi|Z))}{\Omega(\bar{E}, Z)}, \quad (2)$$

that will be named cumulant density operator (CDO) where  $\bar{E}$  is a parameter. In the former  $\omega$  is defined as:

$$\omega(\bar{E}, Z) = \text{Tr}[\delta(\bar{E} - H(\xi, Z))], \quad (3)$$

where in the latter  $\Omega$  is:

$$\Omega(\bar{E}, Z) = \text{Tr}[\theta(\bar{E} - H(\xi, Z))], \quad (4)$$

with  $\theta$  the Heaviside step function and  $\text{Tr}$  is intended as a trace of the corresponding quantum operator, or a normalizing summation over all energy states.

If we use these two different density operators to get the PDF over the DOS of the phase space, fixed the internal energy control parameter,  $\bar{E}$ , we get two uniform distributions:

$$\rho_M(\xi|\bar{E}, Z) \rightarrow \frac{1}{|\Gamma_{E=\bar{E}}|} \equiv \frac{1}{|\Gamma_B|}, \quad (5)$$

$$\rho_C(\xi|Z; \bar{E}) \rightarrow \frac{1}{|\Gamma_{E \leq \bar{E}}|} \equiv \frac{1}{|\Gamma_{GH}|}, \quad (6)$$

where the subscripts  $B$  and  $GH$  stand for Boltzmann and Gibbs-Hertz. The difference is that the Boltzmann PDF is uniform over all the states of the system with energy equal to  $\bar{E}$ , while the Gibbs-Hertz is uniform over all states with energy  $E \leq \bar{E}$ . If we insert the Boltzmann PDF inside the standard Shannon entropy functional,

$$S = -k_B \text{Tr}[\rho \ln \rho], \quad (7)$$

where  $k_B$  is the Boltzmann constant and  $\rho$  the density operator we get the Boltzmann entropy,

$$S_B = \ln |\Gamma_B| = \ln \epsilon \omega(\bar{E}). \quad (8)$$

As pointed out in [6], an infinitesimal  $\epsilon$  is actually needed in order to give a "volume" to the shell of states with energy just equal to  $\bar{E}$ . It is important to stress that in equilibrium and without any dissipation, under ergodic assumptions, these are the states effectively explored by the system during time evolution.

If the Gibbs-Hertz PDF is inserted in the Shannon functional, we get the correct Gibbs-Hertz entropy, as presented in [6]:

$$S_{GH} = \ln |\Gamma_{GH}| = \ln \Omega(\bar{E}). \quad (9)$$

Thus we observe that the correct Gibbs-Hertz entropy for the microcanonical ensemble does not need the invention of a novel entropy functional, beyond the conventional Shannon entropy. What is really needed is the correct PDF.

Information Theory [7] provides a perfectly consistent framework inside which thermodynamics can be developed, but it lacks an important piece of knowledge that can only come from physical considerations. Information Theory is based on functionals, such as the Shannon entropy [8], from which the entire theory is derived. For example two of the main achievements of information theory, namely channel capacity and rate distortion theory, are nothing else than respectively maximizing or minimizing a mutual information functional. However, information theory has nothing to say about the shape of the PDF, the basic ingredient of the entropy functional. The theory just predicts some statistical/probabilistic aspects of the system once its PDF is known or assumed. The only constrain is that the PDF has to be properly normalized, as any PDF should be, but this leaves infinite classes of functions fulfilling this requirement.

Thus, information theory requires a correct PDF that can only be obtained by empirical considerations, experimental evidences or numerical simulations based on the underlying microscopic physics.

In the case of a system in a microcanonical ensemble, physical considerations based on the fulfillment of the laws of thermodynamics and the equipartition theorem, bring to conclude that the correct PDF is the Gibbs-Hertz and not the commonly used Boltzmann PDF, although the subtle difference between the two is not usually perceived since in normal systems, for which the density of states grows monotonically with energy, all the contribution to the Gibbs-Hertz entropy is given by states with energy  $E = \bar{E}$ , essentially recovering the Boltzmann result [9]. This becomes asymptotically correct in the thermodynamic limit where the number of states with energy  $E < \bar{E}$ , for a monotonic DOS, becomes negligible, so that  $\Omega$  converges to  $\omega$  and the Gibbs-Hertz entropy becomes the Boltzmann entropy. Several alternative forms of PDF are discussed in [6], where it is shown that all fall into some contradiction when compared to physical reality. However, this asymptotic equivalence is only an approximation which must be taken with caution and forbids general conclusions. Among the others, systems where Boltzmann MDO fails are small systems, for which the thermodynamic limit does not hold [10] or those characterized by an anomalous DOS, i.e., DOS that are not simply growing monotonically with energy, but for instance have a maximum and then decrease to zero.

However, this rises an important question: why the CDO is correct, considering that a closed system without dissipation can only "explore" states with  $E = \bar{E}$ ?

A practical answer could be that the CDO is the one which gives the right PDF and the correct (Gibbs-Hertz) thermodynamic entropy and any further consideration could be put aside. The thermodynamic laws should dic-

tate the correct PDF and not any other assumption.

A deeper understanding necessarily involves the fact that a perfectly conservative system is only an idealization of reality. Equilibration itself requires dissipation. The MDO (leading to Boltzmann PDF), by sampling only states with  $E = \bar{E}$ , lack any information about the thermodynamic inequivalence between higher and lower energy states involved in the relaxations. As pointed out correctly in [6] "A system occupying the ground state can be easily heated (e.g., by injecting a photon), whereas it is impossible to add a photon to a system in the highest energy state. The Gibbs-Hertz entropy reflects this asymmetry in a natural manner".

For the moment let's think about a simple anomalous DOS starting at  $E = 0$  with  $\text{DOS}(0) = 0$ , reaching a maximum and then going to zero, and let assume that our system is in a microcanonical ensemble. It is clear that if we use the Boltzmann PDF and substitute it into the Shannon entropy we get a non monotonous entropy. Computing the system temperature using the traditional expression,

$$\frac{1}{T} = \frac{\partial S}{\partial E}, \quad (10)$$

leads to an apparently negative temperature, whenever  $\bar{E}$  is larger than the DOS maximum. This has started a debate in the literature about the interpretation of this result trying to give significance to negative temperatures in general. However this result is wrong.

The problem is precisely that the Boltzmann PDF assumes a sort of symmetry between low and high energy states as it depends only on the DOS value. In practice there is no difference if a system is in a high or low energy with respect to the DOS. Instead, by using the correct Gibbs-Hertz PDF one gets a monotonous entropy, regardless the shape of the DOS. A direct consequence is that the temperature remains always positive.

There is a last point to clarify. If the correct microcanonical PDF is that of Gibbs-Hertz, why in many averaged quantities we use safely the Boltzmann PDF? The answer is simply given by analyzing how the averages are taken (see for example eq. 11 in [6] associated to the equipartition theorem):

$$T_{GH} = \left\langle \xi_i \frac{\partial H}{\partial \xi_i} \right\rangle_{E=\bar{E}}, \quad (11)$$

where  $\xi_i$  is any of the  $i^{th}$  degrees of freedom describing the state  $\xi$ , the subscript  $GH$  stresses the fact that temperature is computed using the derivative of the Gibbs-Hertz entropy and the brackets  $\langle \dots \rangle$  means ensemble average. We observe that the average is taken under the constrain  $E = \bar{E}$  and we notice that this is equivalent to saying that the average is taken over a conditioned PDF of the original Gibbs-Hertz PDF. In fact, it is trivial to see that we obtain the MDO from the CDO (and the Boltzmann PDF from the Gibbs-Hertz PDF) just by making the conditioning,

$$\rho_M(\xi) = \rho_C(\xi|E = \bar{E}). \quad (12)$$

In practice we can drop the redundant symbol,  $E = \bar{E}$ , at the averaging brackets  $\langle \dots \rangle$ , as it is redundant when using the conditioned MDO in the average. This subtle result, coupled to the asymptotic equivalence between Boltzmann and Gibbs-Hertz PDFs in the thermodynamic limit, has been the source of a large confusion and a widespread use of the Boltzmann PDF taken as generally valid.

The major conclusion of this section is that the Shannon entropy functional for the thermodynamic entropy seems to be valid in more general cases, provided the correct PDF is used. We have also seen that the Boltzmann PDF is an asymptotic approximation of the Gibbs-Hertz PDF. Furthermore the Boltzmann PDF is correct when used in averaged quantities because it is nothing else than the conditioned Gibbs-Hertz PDF on the surface  $E = \bar{E}$ . However, as we will show in the next part of this work, it is possible to have genuine situations where the temperature becomes negative, but this requires non-equilibrium conditions.

### III. NEGATIVE TEMPERATURE, DARK ENERGY AND CARNOT CYCLE EFFICIENCY

This section is more speculative, but we believe it can help to clarify several aspects concerning inverted populated systems and, more generally, all those indicating the existence of a negative temperature and using the equipartition relation a consequent "dark energy".

First of all we will enlist our position about the three different topics and then explain in more detail:

- Existence of negative temperature? YES;
- Dark Energy? NO;
- Carnot cycles with efficiency larger than unity? TAKEN VERY CAREFULLY.

In order to explain our position we will mention the work made in [11]. In their paper the authors discussed the thermodynamics of a particle in a noisy environment described by a Langevin equation. They assumes that the particle starts with an energy larger than the equilibration energy and analyze the exchange of heat and work between the particle and the environment.

It is clear that such a system describes a particle in a canonical ensemble. They show that until the particle is out of equilibrium, its state can be described by two different temperatures, one simply related to the particle kinetic energy,  $k_B T_{ET} \propto \bar{E}$ , and the other computed using  $T_{ED} = dE/dS$ . The first temperature is fundamentally linked to the average energy per degree of freedom of the system and thus is always positive and related to the equipartition theorem. This temperature definition is always possible even under non-equilibrium conditions, since the average energy per degree of freedom is always a well-defined quantity. The second temperature is a thermodynamic temperature, that requires stretching the

concept of entropy also to systems out of equilibrium and in many cases this extension is still questionable. In their work Narayanan and Srinivasa assume that the form of the Shannon is still valid in the case of a non equilibrium steady state (NESS), in which a distribution function is meaningful. Then, they link  $dE/dS$  with the average curvature of the PDF,  $kT_{ED} = \langle \nabla H \nabla H \rangle / \langle \nabla^2 H \rangle$ , where  $H$  is the Hamiltonian of the system, leading, via the De Bruijn's identity, to an expression related to the Fisher information [11].

We do not want to discuss here the general validity of this approach, but we find it elegant and meaningful. Assuming this is correct, at least for the particular system analyzed there, we want to concentrate on its consequences.

Calling  $T_0$  the environment temperature, it is important to notice that in equilibrium  $T_{ED} = T_0 = T_{ET}$ . This result, apparently obvious, is in fact quite special to the higher constrain of the equilibrium state [12, 13], and explains why temperature is such a useful concept in equilibrium. It also explains why temperature is still useful in the microcanonical ensemble, where it is not a control parameter.

To this result we add the following finding. Consider the average energy,  $\langle E \rangle = \sum_i p_i E_i$ , and entropy,  $S = -k_B \sum_i p_i \ln p_i$ , and a small perturbation to the distribution probability of the general form

$$p'_i = p_i + \epsilon \sum_k \pi_{ik} p_k, \quad (13)$$

where  $\epsilon$  is infinitesimal and  $\pi_{ik}$  a general convolution matrix, subject to  $\sum_i \pi_{ik} p_k = 0$ , necessary to preserve the condition  $\sum_i p'_i = 1$ . Assuming further that the perturbation on  $S$  and  $\langle E \rangle$  does not perturb the state energies,  $E_i$ , and that the equilibrium distribution is the canonical  $p_i = \exp(-\beta E_i)/Z$ , it is not difficult to find that

$$\frac{dS}{d\langle E \rangle} = \frac{\delta S}{\epsilon} \frac{\epsilon}{\delta \langle E \rangle} = \frac{1}{T}, \quad (14)$$

completely independent on the form of the perturbation  $\pi_{ik}$ . This shows that in equilibrium conditions, no matter how physical thermometers couple to a system, they will all agree in measuring the same temperature.

Not surprisingly, under non-equilibrium conditions, we have in general  $T_{ED} \neq T_{ET} \neq T_0$ . What does this mean? It simply means that in non-equilibrium conditions the entire concept of temperature must be taken with care. Different ways to compute temperature are connected to different aspects of the thermodynamics of the system under consideration and a general definition is probably not possible. While  $T_{ET}$  is linked to the energy content of the system,  $T_{ED}$  is related to a curvature of the PDF in phase space. An interesting result of [11] is that the amount of work and heat exchanged between the particle and the environment are related (proportional) to temperature differences as,

$$\Delta Q \propto (T_0 - T_{ET}), \quad (15)$$

$$\Delta W \propto (T_{ED} - T_{ET}). \quad (16)$$

Despite this result lack generality, we think the reasoning gives useful insights and these final expressions are noteworthy, showing that different temperatures can be used in a thermodynamic sense to define the direction of heat and energy fluxes.

Now let's focus on the problem of an inverted populated systems in steady state. We can consider two possibilities: a) the system is in an inverted populated state, but it is in equilibrium conditions, b) the system is in a NESS forced by some external drive [14].

In the first case we must have  $T_{ED} = T_{ET} > 0$ . This condition is the one discussed in [6] by Hilbert and coworkers and the conclusion is that the system must be in a microcanonical ensemble and the temperatures is unique and positive. A corollary is that no dark energy exists and the efficiency of any Carnot cycle where one of the bath is an inverted populated system is bound to  $\eta \leq 1$ , with:

$$\eta = 1 - \frac{T_{cold}}{T_{hot}}. \quad (17)$$

We do not further discuss this case as all the conclusions in [6] are correct and widely explained there.

When there is an external drive or a feedback machine, forcing the system out of equilibrium, then, in general,

- $T_{ED} \neq T_{ET}$ ;
- The system is not in a microcanonical ensemble as an external feedback has to interact with the system in order to preserve its NESS.

In this case there are no fundamental reasons preventing  $T_{ED}$  to become negative since the drive or the feedback can push the system in a state where the PDF inserted into the Shannon entropy leads to an entropy function non monotonous with energy.

As we have previously discussed, in the equilibrium this is forbidden as there is an intrinsic thermodynamic difference between occupying low or high energy states. We can think that an external drive, making work, can circumvent this asymmetry leading to a negative  $T_{ED}$ . However, we notice that if  $T_{ED} < 0$ , since  $T_{ET} > 0$  (always), necessarily  $T_{ED} \neq T_{ET}$ . We also notice that using the results of [6], the special condition  $T_{ED} < 0$  is only possible under non-equilibrium conditions. The final observation of this discussion is that although  $T_{ED} < 0$  may have a meaning, this temperature is related to entropy and state distribution but is generally unrelated to the energy content of the system, ruling out the existence of dark energies.

Let's now discuss the Carnot cycle efficiency of a cycle between two reservoirs in equilibrium, one of which has an inverted population condition. We call  $R_{st}$  the standard reservoir,  $R_{inv}$  the reservoir with inverted population and  $S_1$  the system coupling in alternation with the two reservoirs along the Carnot cycle.

Also in this case, for the inverted population reservoir, we consider the two possibilities: equilibrium/microcanonical or NESS. If  $R_{inv}$  is in thermodynamic equilibrium, then (assuming as usual a weak coupling to  $S_1$ ), it must be characterized by  $T_{inv} > 0$ , hence  $\eta = 1 - T_{inv}/T_{st} \leq 1$ . In the case of a NESS and  $T_{ED} < 0$ , then  $R_{inv}$  must be under non-equilibrium conditions. Apparently in this case we may conclude  $\eta > 1$ , however the traditional definition of Carnot efficiency, equation (17), must be taken with care in this case. Even assuming (17) is still correct, we have already concluded that under these conditions  $T_{ED} \neq T_{ET}$ , therefore it is not clear which temperature must be used in (17). Although there are indications that the correct Carnot efficiency can be obtained for a NESS system using  $T_{ED}$  [15], this result is not general, and it has been shown only for the case  $T_{ED} > 0$  and may not apply to all NESS systems, especially those with a negative  $T_{ED}$ . In fact the two reservoirs  $R_{st}$  and  $R_{inv}$  and the system  $S_1$  cannot make an isolated engine since an external drive or a feedback is certainly needed to keep  $R_{inv}$  in its inverted NESS. Any such driver is making work on the system or producing a large amount of entropy to accomplish this task. In accounting the total Carnot efficiency, we cannot forget this work. Therefore, the surprising result  $\eta > 1$  is meaningless. This simply means that in doing the energy accounting we are disregarding the energy flux between driver and  $R_{inv}$ , which continuously makes work on  $R_{inv}$ , increasing its own entropy to keep  $R_{inv}$  into the inverted state. The entropy production associated makes the total efficiency to inevitably drop below unity. So, unfortunately, no dark energy and perpetual motion are possible.

#### IV. CONCLUSION

In this paper we have tried to clarify some points about the debate between Boltzmann, Gibbs-Hertz and Shannon entropy and the concepts of negative temperature, dark energy and Carnot efficiencies larger than one in inverted populated systems.

We agree that in a system in equilibrium and in a microcanonical ensemble the Gibbs-Hertz entropy is the correct thermodynamic entropy, however this does not contradict the fact that Shannon entropy is still the right functional for thermodynamic entropy in general. It is just telling us that we have to choose the right probability density function. In particular in the microcanonical ensemble the correct one is the Gibbs-Hertz uniform density function derived from the cumulant density operator. This is also the right density function because it produces the entropy with the correct "knowledge" of the directionality in energy state for which high energy states

are not equivalent to lower energy states. Moreover, the Gibbs-Hertz entropy satisfies all the thermodynamic laws and the equipartition theorem.

The source of the confusion is that for other constrained averages in the microcanonical ensemble another probability density function is used, the Boltzmann density, derived from the microcanonical density operator, which incidentally becomes almost equivalent to the Gibbs-Hertz density function for standard density of states, especially in the thermodynamic limit. However, the discussion of anomalous density of states [6] has shown that the Gibbs-Hertz is correct and the Boltzmann is wrong in more general cases. The Boltzmann uniform distribution is anyway correct for all the averaging which require a conditioned Gibbs-Hertz distribution, in particular when we require  $E = \bar{E}$ , with  $\bar{E}$  the energy of the system fixed as control parameter. This shows that we should be careful in choosing the correct density function for calculating different averages.

The second part of this work was focused on analyzing the thermodynamics of inverted populated systems. We have pointed out that inverted populated systems can exist in steady state only in two possible conditions: equilibrium or non-equilibrium steady state. In the first case, as demonstrated by [5], the system must be isolated (microcanonical ensemble), the correct entropy functional is the Gibbs-Hertz which leads always to a positive defined temperature. This forbids any dark energy, negative temperature and it shows that if the system is used like a reservoir in a Carnot engine leads to a maximal unitary efficiency.

In the second case (non-equilibrium steady state), we have shown that there are evidences that point on the fact that temperature is not a single value and different ways to compute this parameter can lead to different values. In particular we can indeed keep the system in a way to get a negative temperature obtained from the derivative of entropy w.r.t. energy. However, this means that this temperature has nothing to do with the temperature derived from the equipartition theorem and in particular with the energy content of the system. So again no dark energy can exist.

Concerning the Carnot efficiency in the presence of non equilibrium steady state with an inverted population reservoir and a negative temperature, we have argued that we should be careful as the entire concept of Carnot efficiency equation cannot be taken for granted. But even assuming it is correct, obtaining an efficiency larger than one does not have any meaning, simply because we are not taking into account the cost of keeping one of the two reservoirs in non equilibrium conditions. Thus it would be better to call such parameter with a different name, such as "partial efficiency", in order to clearly distinguish it from the real efficiency.

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